

MOVPE Growth of $\text{GaAs}_{1-x}\text{N}_x$ Alloys

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Abstract

$\text{GaAs}_{1-x}\text{N}_x$ ($x \leq 0.51\%$) dilute alloys have been grown on GaAs substrates by metalorganic vapor phase epitaxy (MOVPE) using 1,1-dimethylhydrazine (DMHy) as the N source. Solid versus vapor composition for the $\text{GaAs}_{1-x}\text{N}_x$ growth shows an extremely low solid solubility of N in GaAs, and shows a tendency for phase separation where GaN coexists. The incorporation of N in GaAs is due to non-equilibrium circumstances realized in MOVPE. Low-temperature photoluminescence shows a red shift of the spectrum with increasing N content in the alloy. The energy gap of the $\text{GaAs}_{1-x}\text{N}_x$ alloy is considered to have a large bowing in its composition dependence.

1. Introduction

The alloy system made from GaAs ($E_G = 1.42\text{eV}$) and GaN ($E_G = 3.4\text{eV}$), i.e. $\text{GaAs}_{1-x}\text{N}_x$, has a great possibility to be utilized as a direct gap semiconductor which covers the entire visible wavelength region. This alloy system, however, is considered to have a large miscibility gap, or a low solid solubility, as expected from the structural mismatch between the end components; GaAs is cubic (zincblende) whereas GaN is hexagonal (wurtzite). Hence the growth of the $\text{GaAs}_{1-x}\text{N}_x$ alloys by a near-equilibrium method is far from feasible. This situation is much the same with the growth of the $\text{GaP}_{1-x}\text{N}_x$ alloys [1,2]. Up to now, the $\text{GaAs}_{1-x}\text{N}_x$ alloys with $x \leq 1.4\%$ have been obtained by plasma-assisted MOVPE using NH_3 as the N source [3]. A red shift of the photoluminescence (PL) as well as the absorption edge has been found [3].

In the present study, the $\text{GaAs}_{1-x}\text{N}_x$ alloys have been grown by MOVPE using DMHy as the N source. The N incorporation in the MOVPE growth and the PL properties of the dilute alloys have been examined. The composition dependence of the energy gap is also discussed.

2. Experimental

The $\text{GaAs}_{1-x}\text{N}_x$ alloys were grown on (100) GaAs substrates with a conventional low-pressure (60 Torr) MOVPE system with H_2 carrier. Trimethylgallium (TMG), AsH_3 and 1,1-dimethylhydrazine (DMHy) were used as the Ga, As and N sources, respectively. DMHy was adopted as the N source because it was much easier to dissociate than NH_3 , a conventional N source, at the growth temperatures of 630–650°C, as demonstrated in our GaN growth studies [4]. Prior to the $\text{GaAs}_{1-x}\text{N}_x$ growth, a GaAs buffer layer ($\sim 4000\text{\AA}$) was grown at 700°C. Then the temperature was decreased to 630–650°C for the $\text{GaAs}_{1-x}\text{N}_x$ growth. AsH_3 and DMHy were preflowed for 10 min before the growth. The DMHy/TMG ratio was 140–600, and the AsH_3 /TMG ratio was 1–100, depending on the alloy composition. The growth rate was typically $1\mu\text{m}/\text{hour}$. The thickness of the grown layer was $\sim 1\mu\text{m}$. The alloy composition was determined from the x-ray double crystal (511) diffraction, assuming linear dependence of the lattice constant on composition. Low-temperature PL spectra were measured, using an Ar^+ -laser (488 nm) as the excitation source.

3. Results and Discussion

The relationship between the alloy composition x and the group V vapor composition, $\text{DMHy}/(\text{DMHy}+\text{AsH}_3)$ is shown Fig. 1. The $\text{GaAs}_{1-x}\text{N}_x$ alloys with $x=0.1$ –0.5% were obtained when the DMHy content was 98.5–99.3%. No $\text{GaAs}_{1-x}\text{N}_x$ alloy was grown when the DMHy content was 96.8% or less. When the DMHy content was increased to more than 99.3%, there was a sudden jump in the solid composition, giving a mostly GaN-like phase. Moreover, the GaN-like phase does coexist with the alloys for most growth cases, showing an extremely low solid solubility of N in GaAs, and a tendency for phase separation.

From the delta lattice parameter (DLP) model [5], the solid solution interaction parameter α^S for $\text{GaAs}_{1-x}\text{N}_x$ is estimated as 4.6×10^4 cal/mol, assuming the cubic GaN lattice parameter, 4.5\AA [4]. This value leads to an extremely high critical temperature, $T_c(=\alpha^S/2R) \cong 12000\text{K}$, for alloy stability. It also gives the N solubility $x \leq 10^{-10}$ in GaAs at 650°C. So it can be said that the $\text{GaAs}_{1-x}\text{N}_x$ alloys have been grown under a non-equilibrium condition in MOVPE.

Figure 2 shows the PL spectra of the alloys with $x=0.28\%$ and 0.51% at 17K. A PL spectrum of GaAs ($x=0.0\%$) is also contained for comparison. The PL spectra of the alloys are considered to be made up of the band-edge peak (higher-energy side) and the defect-related peak. No emission peak was observed in the alloys at the band-gap energy of GaAs. The entire spectrum shifts to lower-energy side (red shift) with increasing x .

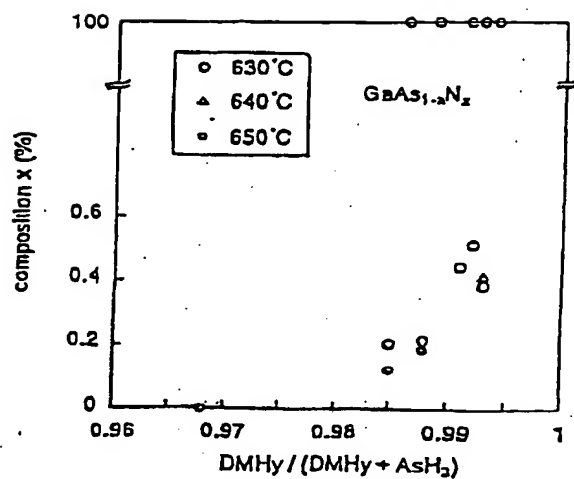


Fig.1 Solid versus vapor composition for $\text{GaAs}_{1-x}\text{N}_x$ MOVPE.

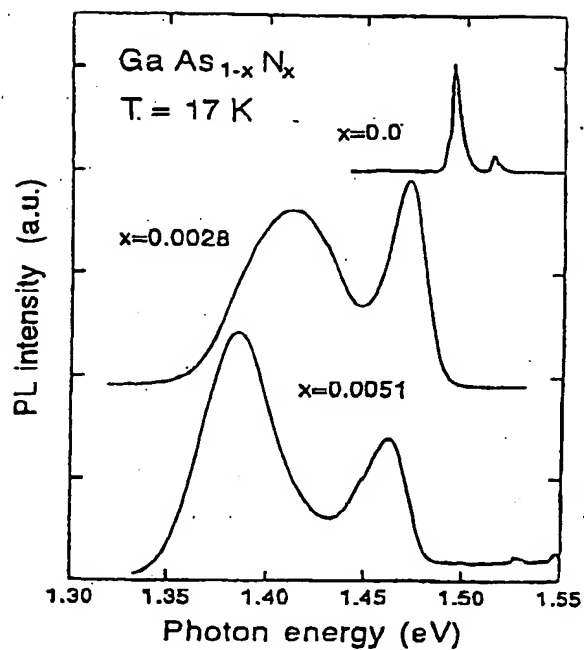


Fig.2 PL spectra of $\text{GaAs}_{1-x}\text{N}_x$ alloys at 17K.

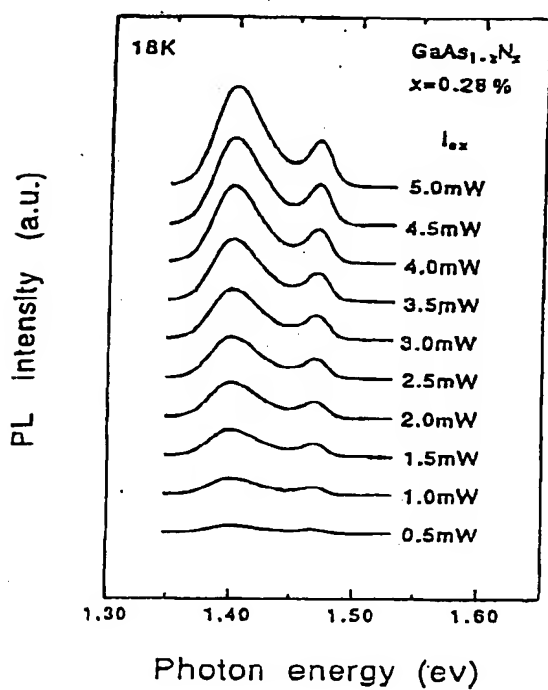


Fig.3 Excitation-power dependence of PL spectra of $\text{GaAs}_{1-x}\text{N}_x$ with $x=0.28\%$.

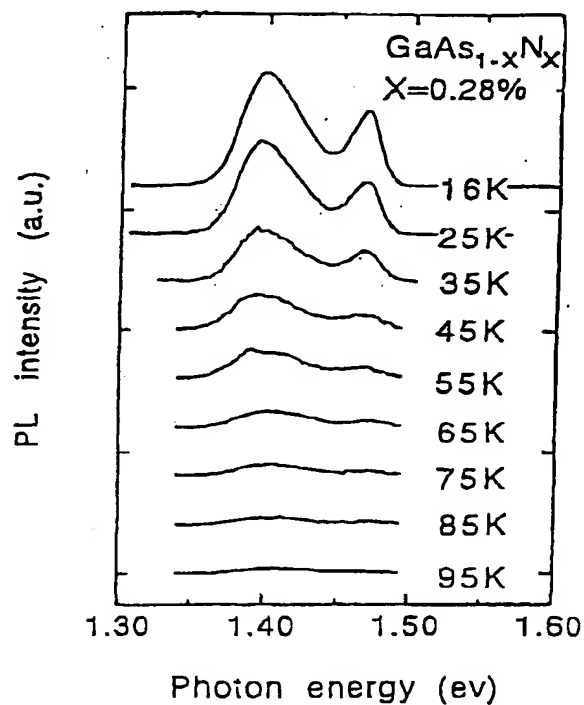


Fig.4 Temperature dependence of PL spectra of $\text{GaAs}_{1-x}\text{N}_x$ with $x=0.28\%$.

The PL spectra of $\text{GaAs}_{1-x}\text{N}_x$ ($x=0.28\%$) alloy at 18K as dependent on the excitation power are shown in Fig. 3. When the excitation power was varied over one order of magnitude, the relative intensities between the two peaks are not much changed without any extra features in the spectra. The temperature dependence of the PL spectrum is shown in Fig. 4. A monotonic decrease in emission intensity is observed up to 95K. These PL behaviors are not contradictory to the band-edge emission. Thus the energy gap of the $\text{GaAs}_{1-x}\text{N}_x$ ($x=0.28\%$) alloy is considered to have an unusually large bowing in its composition dependence. This can be originated from the large difference in the covalent radii between GaAs and GaN.

4. Conclusion

$\text{GaAs}_{1-x}\text{N}_x$ ($x \leq 0.51\%$) dilute alloys are grown on GaAs substrates by MOVPE using DMHy as the N source. The $\text{GaAs}_{1-x}\text{N}_x$ alloy growth shows an extremely low solid solubility and a tendency for phase separation. The non-equilibrium circumstances in MOVPE are essential for the alloy growth. A red shift of the PL spectrum with increasing N content is observed. A large bowing in the composition dependence of the energy gap is assumed.

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